# *Homogeneous and Heterogeneous Reaction and Transformation of Hg and Trace Elements in Combustion Systems*

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# *Pollutants from Coal Combustion*

- Combustion of fossil and waste fuels – release trace elements
- 11 among 187 HAPs
- Coal -major source of several

| **HAPs** | **Estimated US Emissions[1] (1994)** Tons/year |
|---|---|
| Mercury | 51 |
| Beryllium | 7.9 |
| Cadmium | 3.2 |
| Chromium | 62 |
| Lead | 62 |
| Arsenic | 56 |
| Nickel | 52 |

1 *Study of Hazardous Air Pollutant Emissions from Electric Utility Steam Generating Units – Final Report to Congress.* United States, Environmental Protection Agency, February 1998. http://www.epa.gov/ttn/oarpg/t3/reports/eurtc1.pdf

# *Sources of Hg Emissions*

| Mercury Source | Estimated US Emissions (1994-1995)[1] Tons/year |
|---|---|
| Coal Combustion | 73 |
| Municipal Waste Combustor | 30 |
| Medical Waste Incinerator | 16 |
| Other Combustion Sources | 19 |
| Total Combustion | 138 |
| Manufacturing Sources | 16 |
| Miscellaneous sources | 1 |
| Area sources | 3 |
| Total | 158 |

1 *Mercury Report to Congress*, 1997.
http://www.epa.gov/ttn/oarpg/t3/reports/volume2.pdf

Clean Air Mercury Rule - 70% 2018

*(reconsideration "denied" 5/31/06)*

Several states – more stringent rules

- *NY recent*
- *PA*

# *Objectives*

***Identify fate of trace metals***

*- competition between condensation and surface reaction*

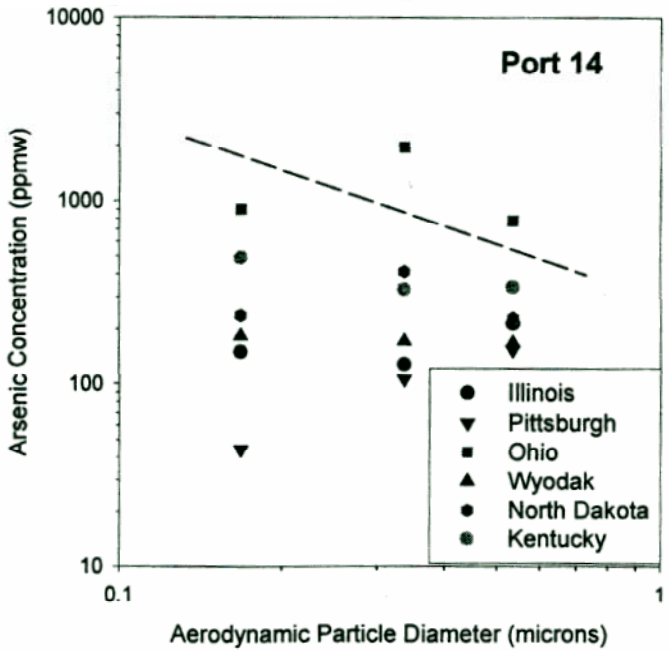
*- Hg heterogeneous pathways*

*- gas-solid reactions for other elements*

# Background

- Particle Size Dependence of Arsenic in Fly Ash
  - Surface condensation (for Kn < 1: $\alpha$ $1/d_p^2$, for Kn >1: $\alpha$ $1/d_p$)
  - Surface reaction ($\alpha$ $1/d_p$)
  - Unvaporized (?)

Sub-micron particles

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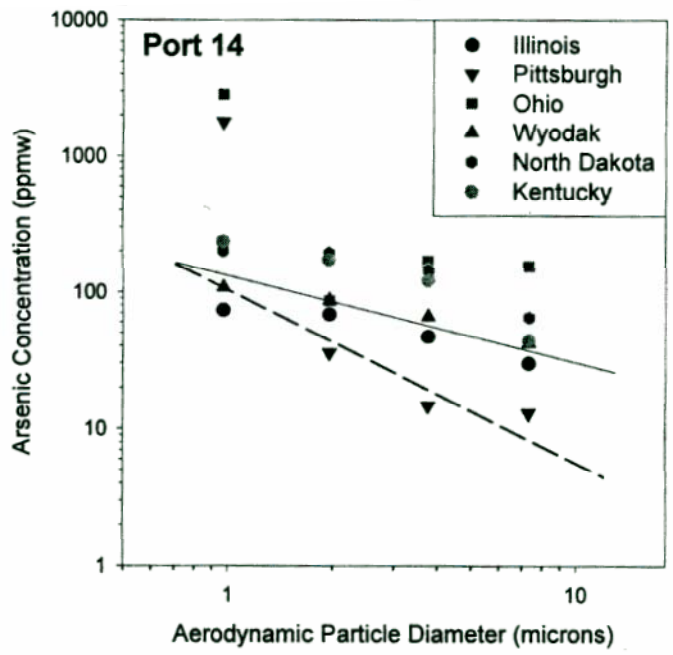


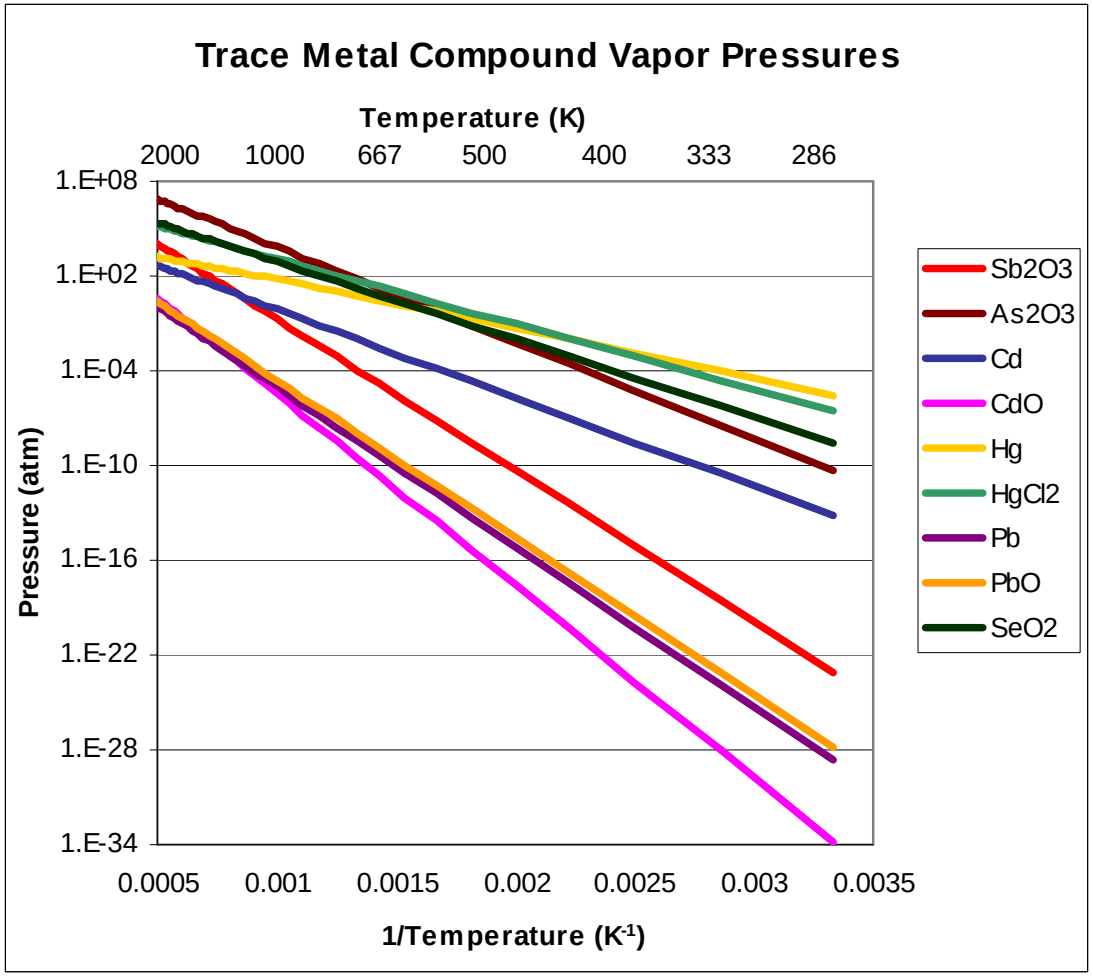

Seames, W. S. *The partitioning of trace elements during pulverized coal combustion.* Ph.D. Dissertation, University of Arizona. 2000.

# *Approach*

- Challenges
  - input/output only
  - scatter in data
  - assumes vaporized species dominant
- Goal – develop generalized, temporal understanding
- Measure surface reaction rates as needed
  - Classify standard fly ash
- Build transient model
  - Competing pathways of metal addition
- Challenges
  - Fly ash composition variation
  - Surface reaction rates

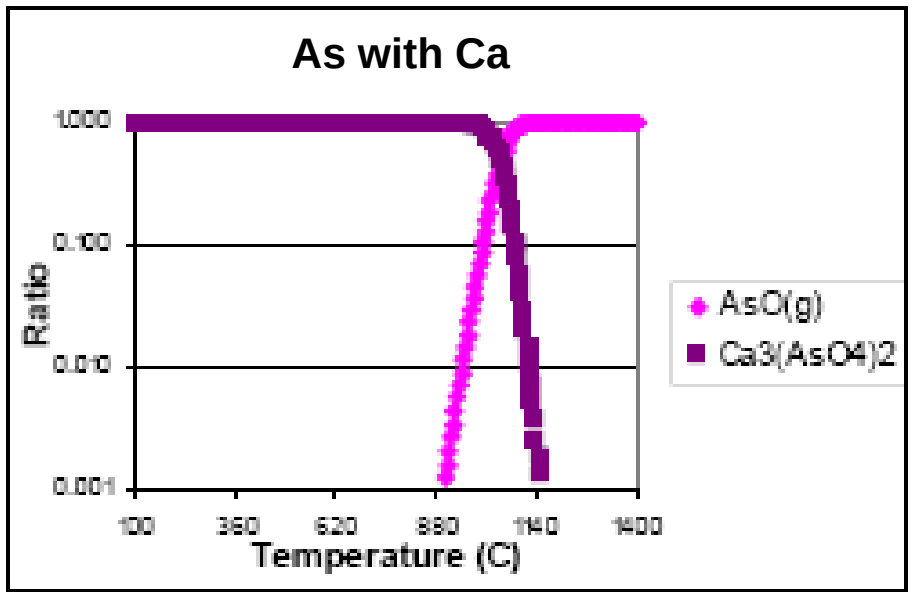
# *Approach: Literature Search*

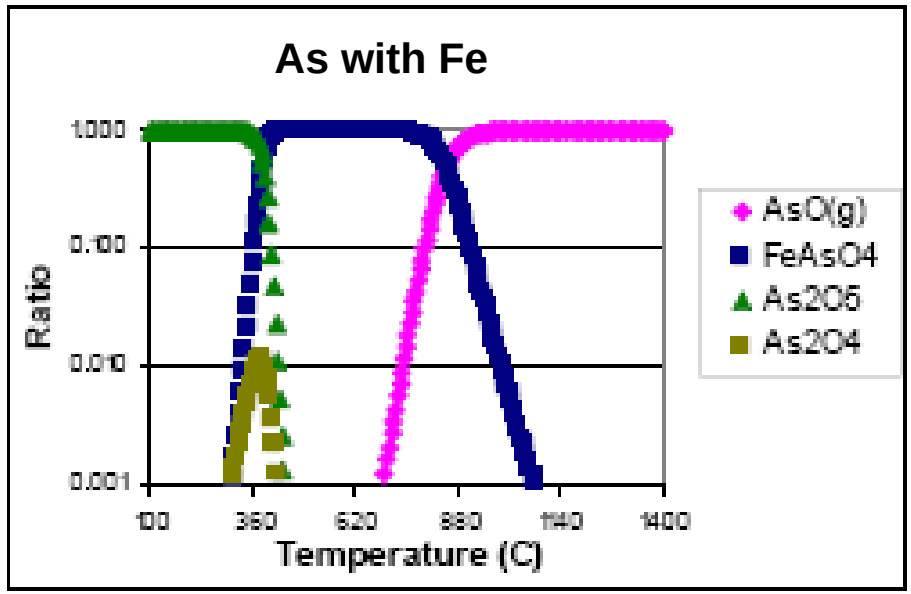
- *Vapor pressure – dominant compounds*
- *Hg, Se, As, Cd most volatile*
- *Existing rxn rate data starting point*



# Partitioning

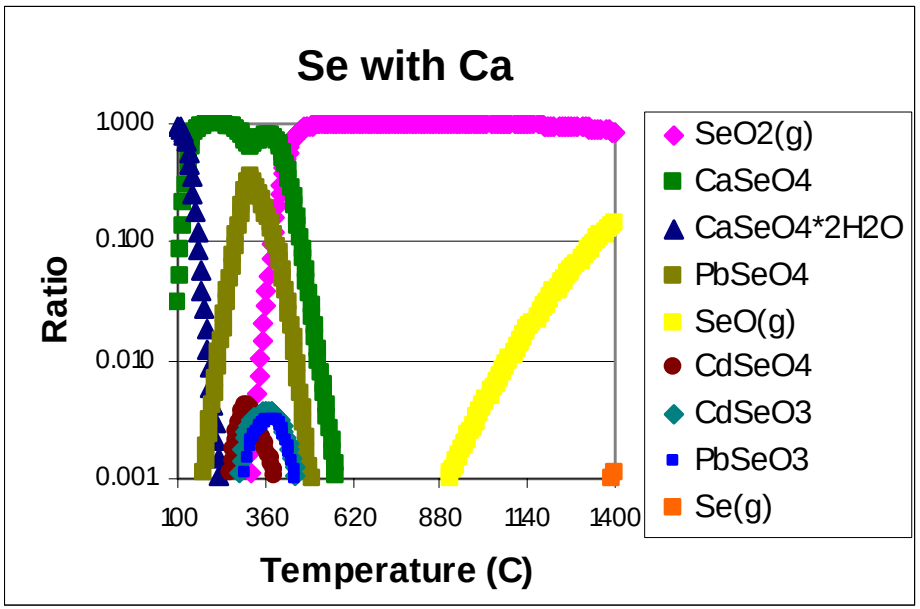
- Equilibrium Calculations
  - Arsenic in Ohio coal

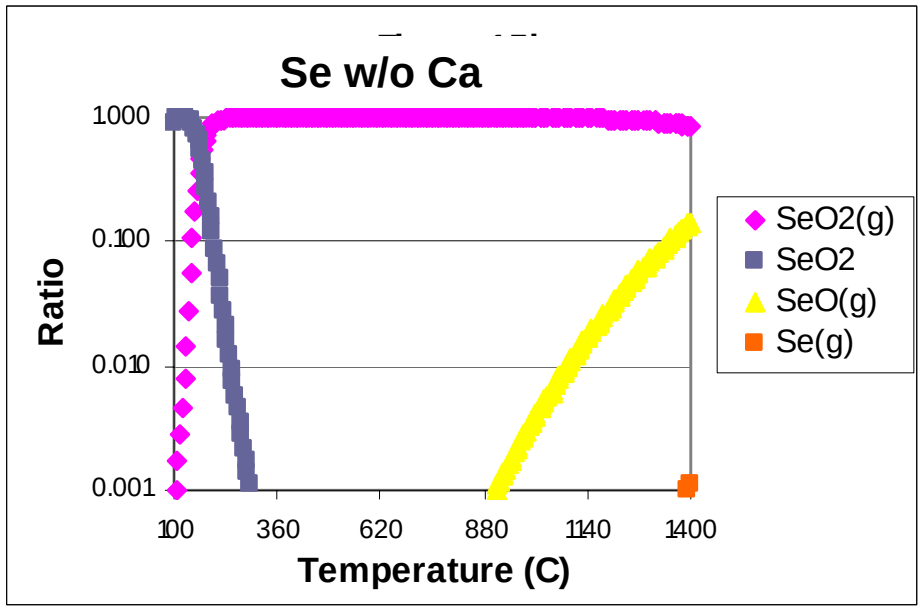


# Approach: Modeling

- Equilibrium Calculations
  - Selenium in Ohio coal



# Model

- Time dependent addition (g metal/s)
- Variables
  - Vaporized metal fraction
  - Surface area factor
  - Quench rate

$$M(d_p) = \frac{6}{\pi d_p^{\,3} \rho_{ash}} \sum_{t=0}^{t=t_f} [K_R(d_p, t) + K_C(d_p, t)] \delta t$$

# *Approach: Modeling*

- Single Particle Model
  - Time-dependent
- Currently studying
  - Kentucky Coal
  - Arsenic
- Addition by reaction

$$K_R = \frac{\pi d_p^{\,2} k_{Ca} P_i}{RT}$$

- Addition by Condensation
  - Continuum Regime

$$K_C = \frac{2\pi d_p D_i (P_i - P_i^{sat})(1 + Kn)}{RT(1 + 1.71Kn + 1.33Kn^2)}$$

  - Free Molecular Regime

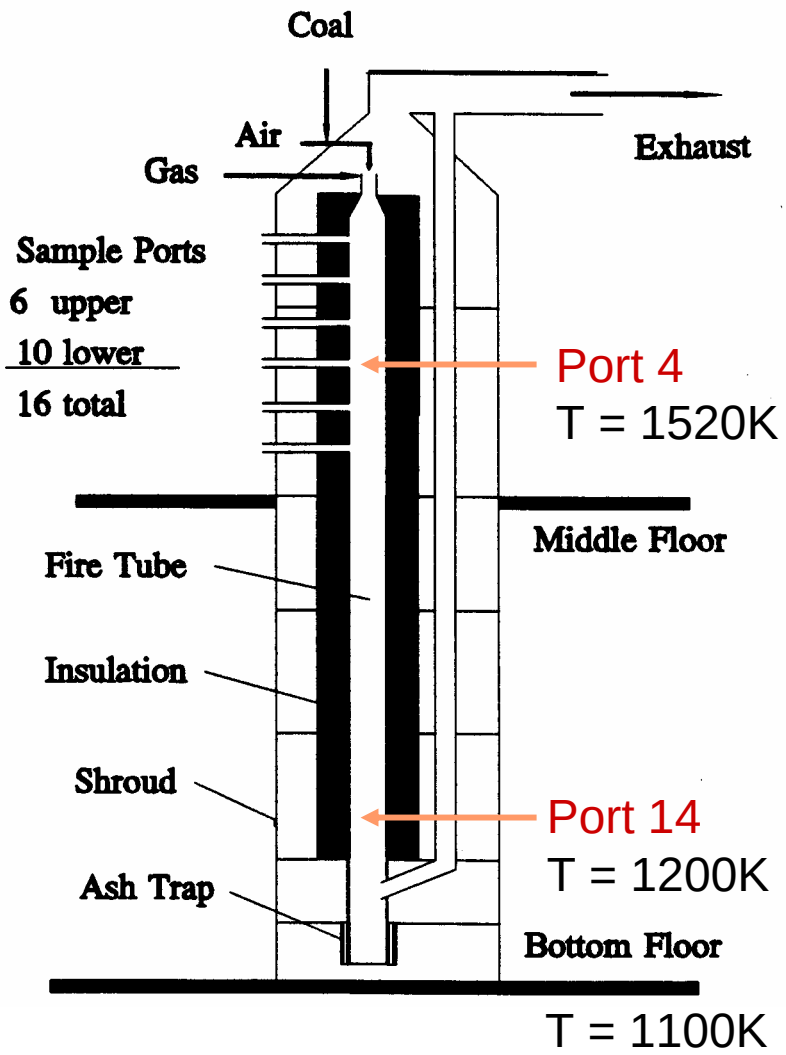
$$K_C = \frac{\varphi \pi d_p^{\,2} (P_i - P_i^{sat}) MW^{\frac{1}{2}}}{(2\pi RT)^{\frac{1}{2}}}$$

# *Model Inputs from Data*

- System
  - Temperature Profile
  - Ash Content
    (g ash/g coal)
  - Metal Content
    (g metal/g coal)
  - Coal and Combustion Gas flowrates
- Ash Characteristics
  - Particle size distribution
  - Calcium oxide mass fraction

# Approach: Modeling

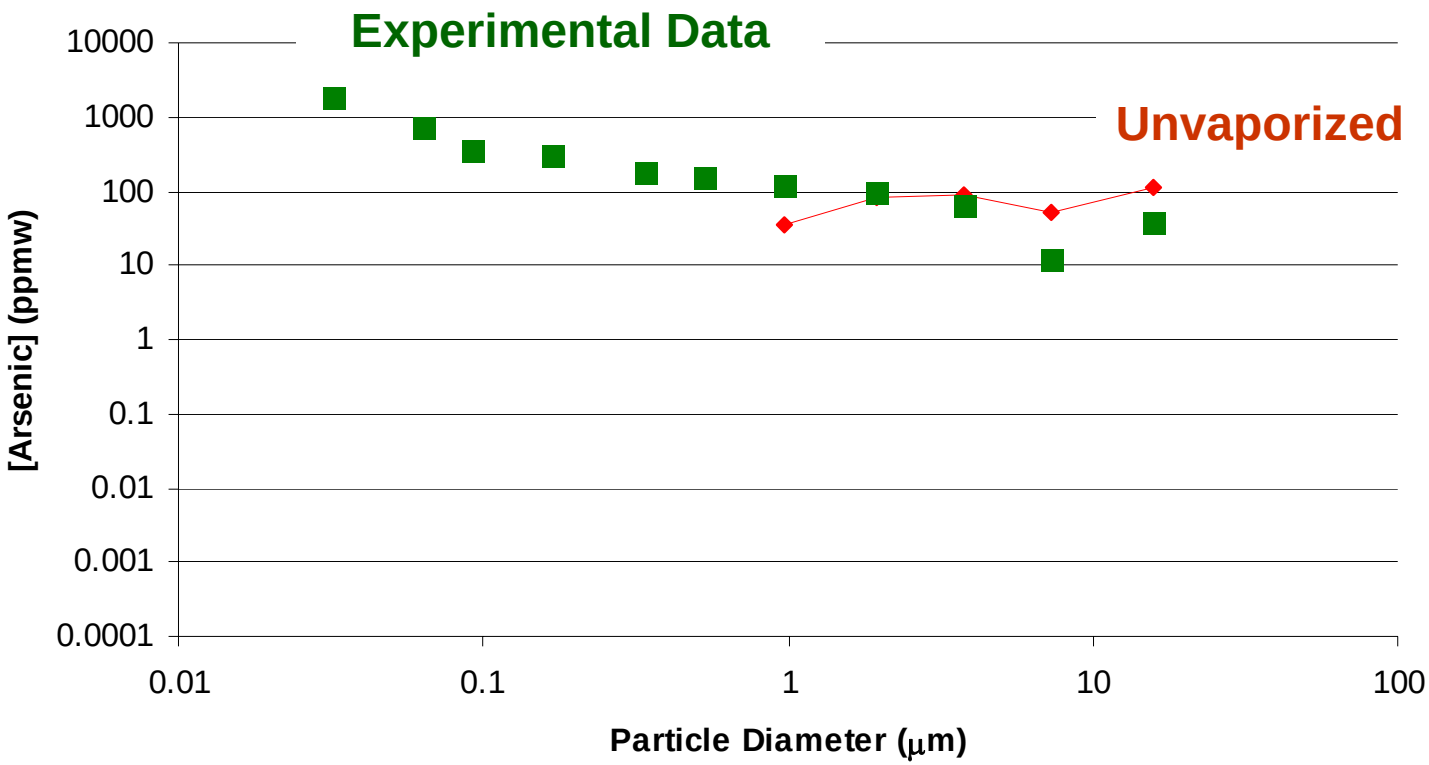
- Experimental data
  - University of Arizona[4]




4 PSI Technology Company. "Transformations of Inorganic Coal Constituents in Combustion Systems." Volume II, November 1992. Contract No. DE-AC22-86PC90751

# Arsenic Addition by Process

- Kentucky Coal
  Port 4, Run 4
  - Vaporized arsenic fraction = 60%
  - Surface area factor = 1
  - Quench Rate = 1000 K/s



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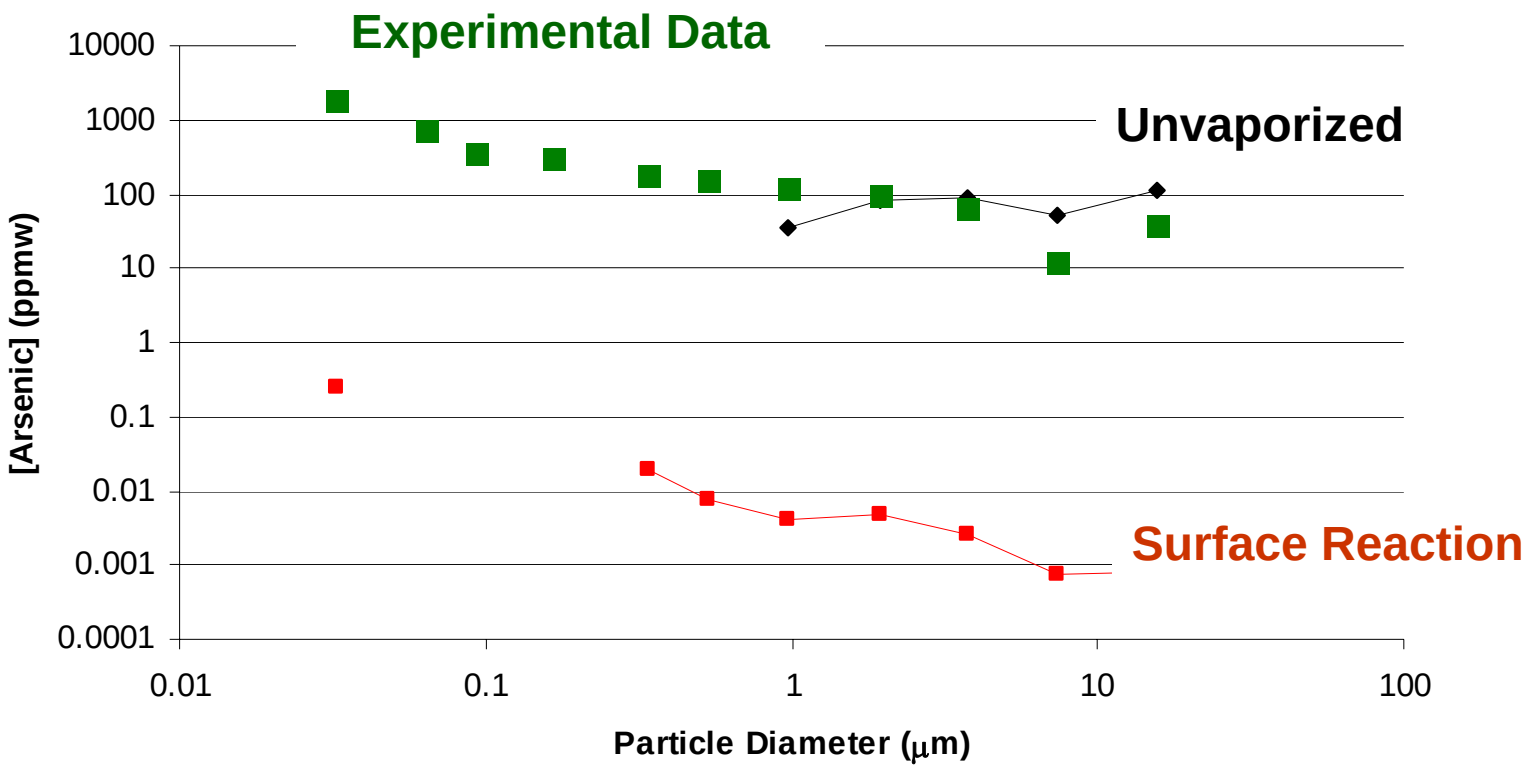

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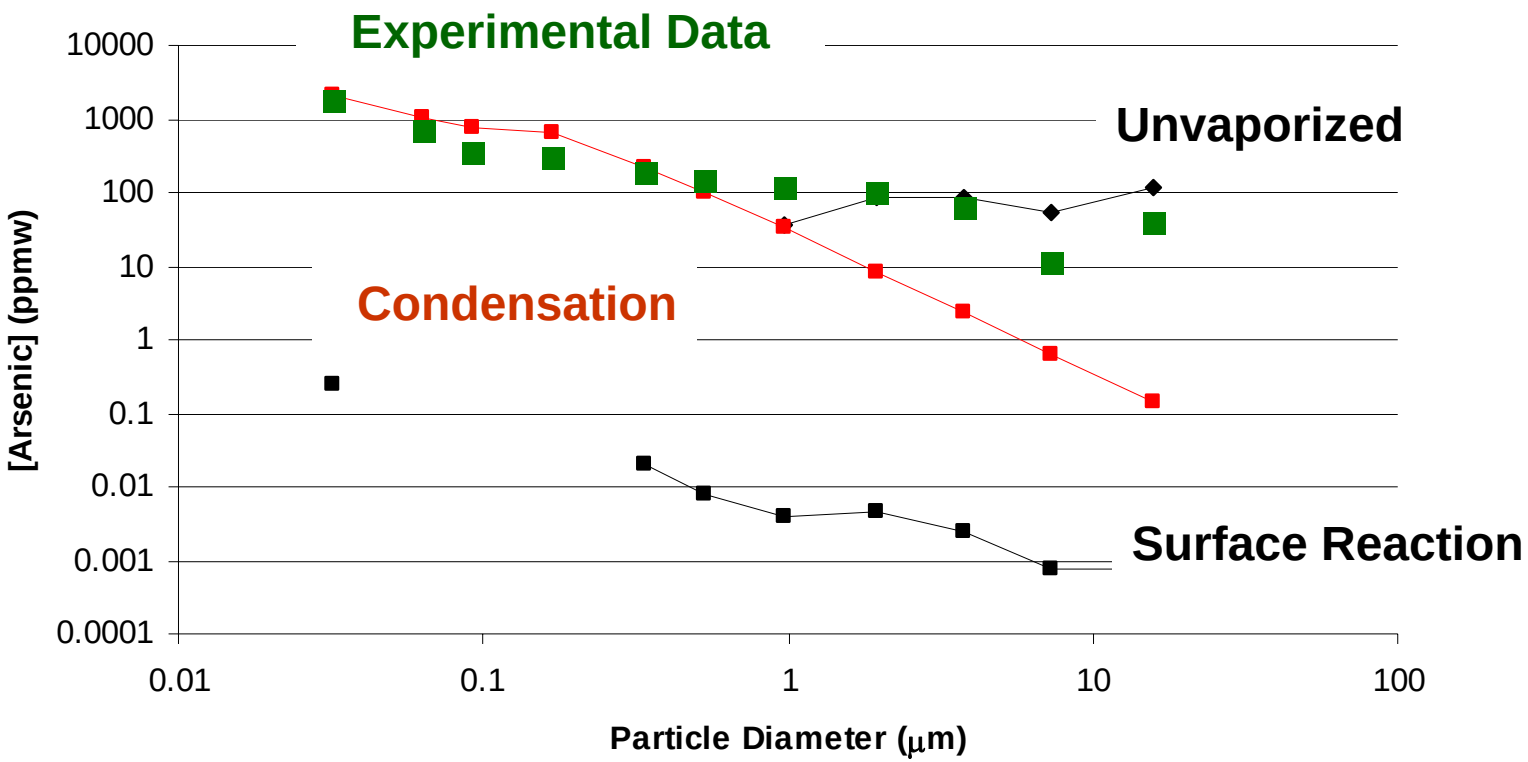

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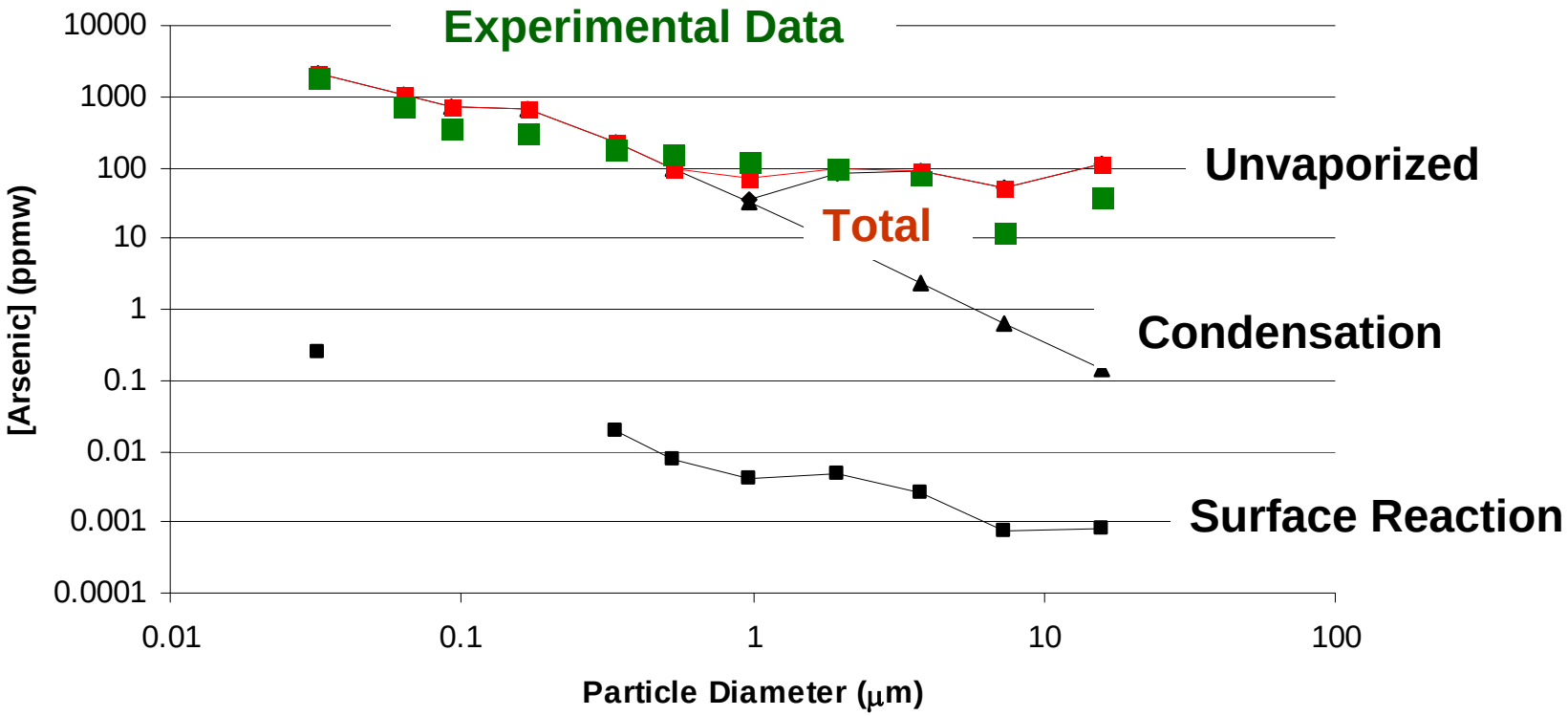
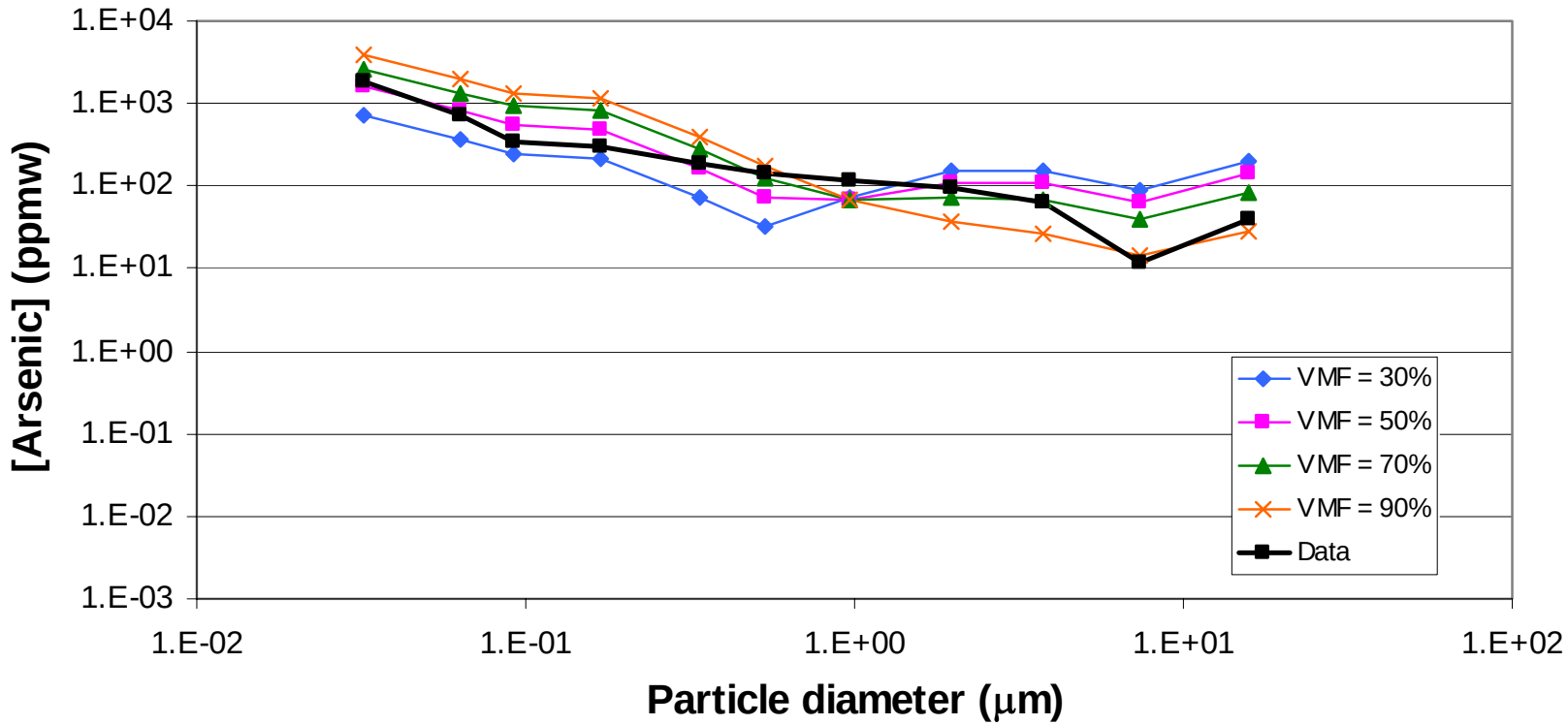



*Condensation plus "apportionment" indicated; surface reaction?*

# Varying Vaporized Metal Fraction

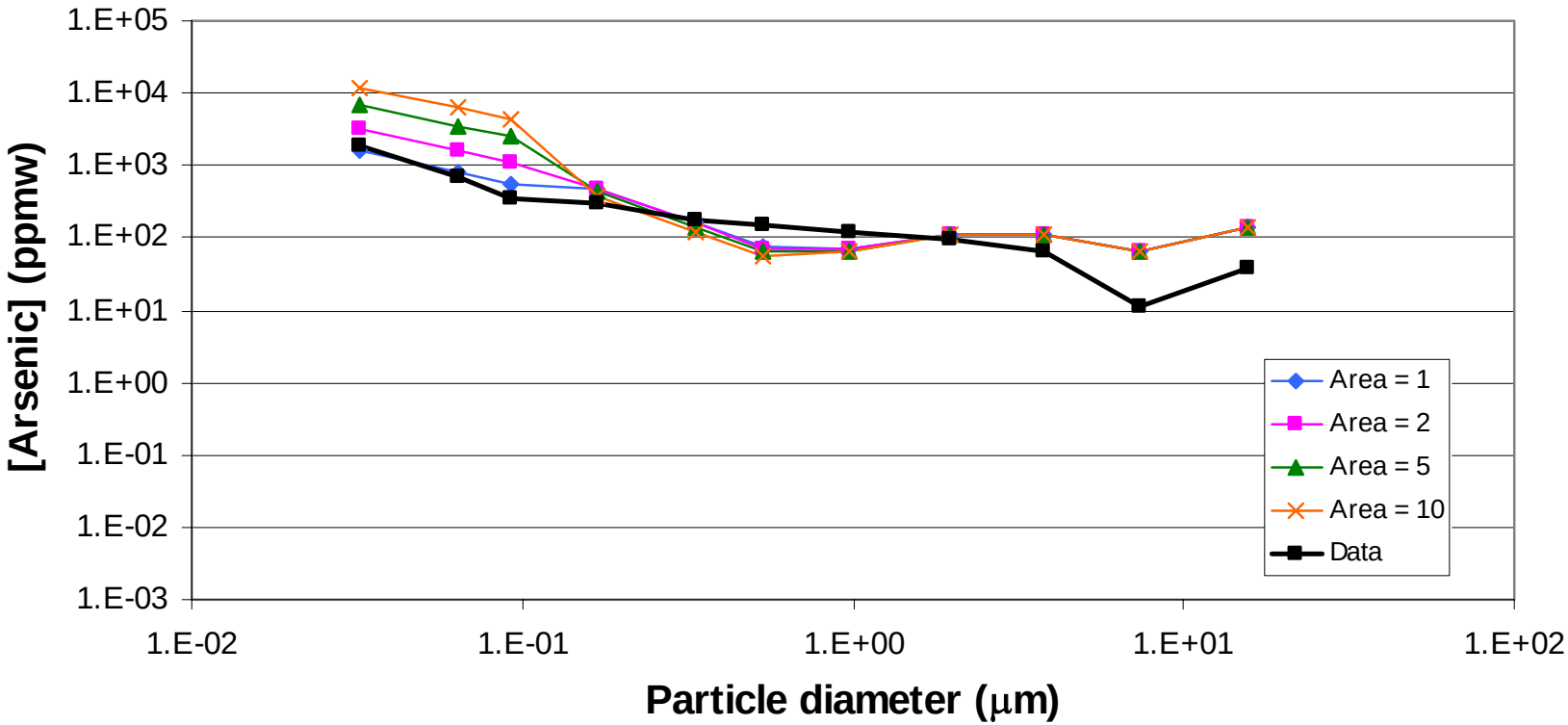
- Kentucky Coal
  Port 4, Run 4
  - Surface area factor = 1
  - Quench Rate = 1000 K/s




*Relative insensitivity to fraction of arsenic vaporized*

# *Varying Surface Area Factor*

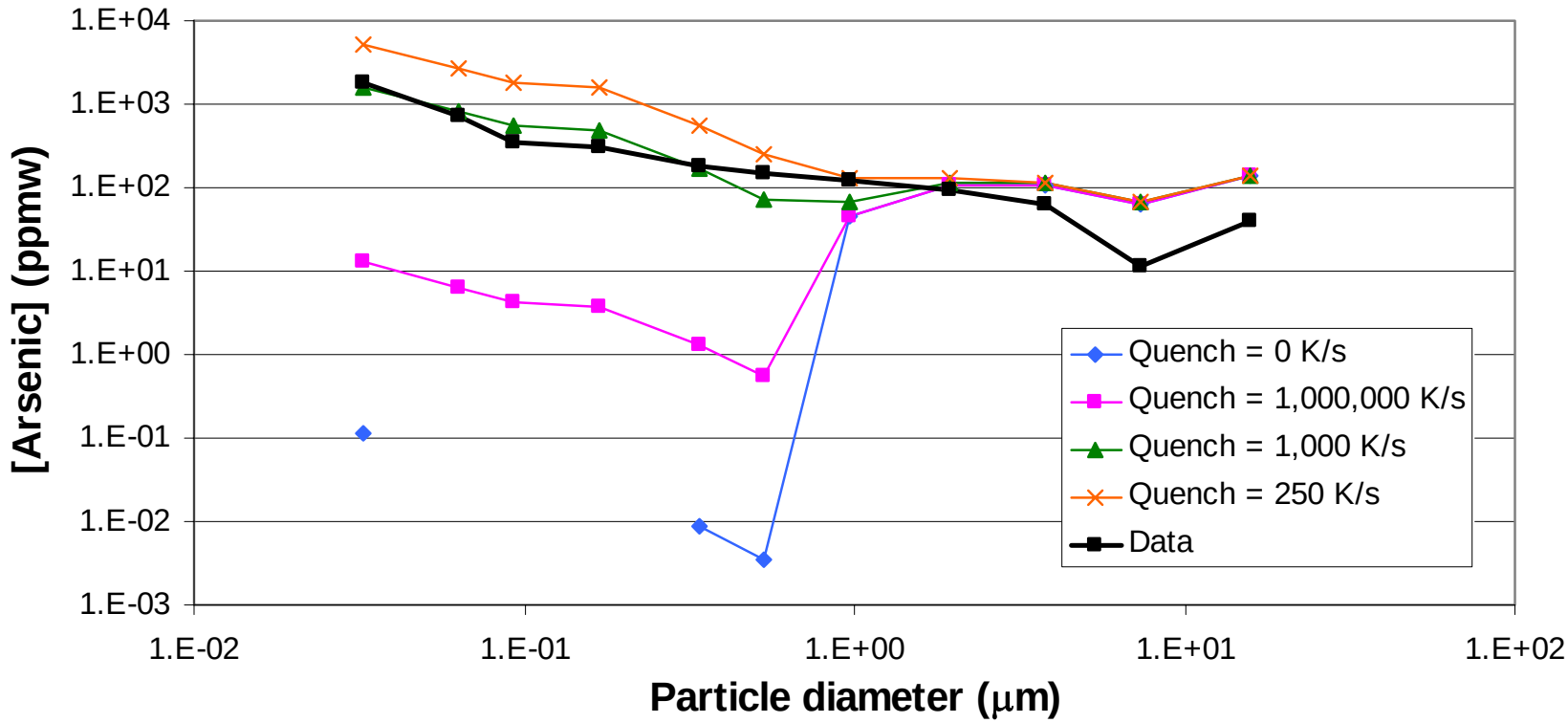
- Kentucky Coal
  Port 4, Run 4
  - Vaporized metal fraction = 50%
  - Quench Rate = 1000 K/s



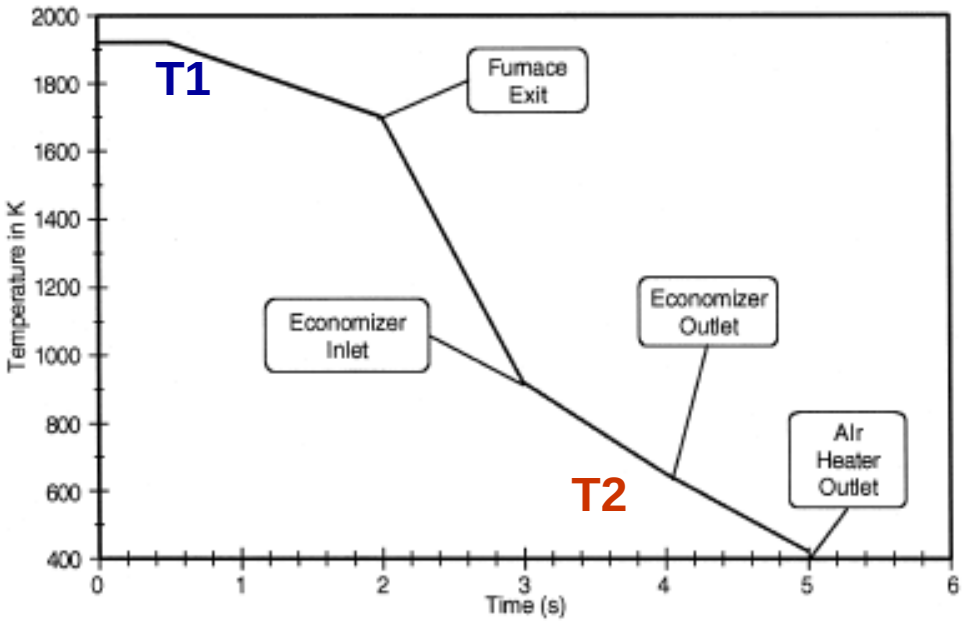

*Additional Asurf increases [As] in submicron fraction as expected*

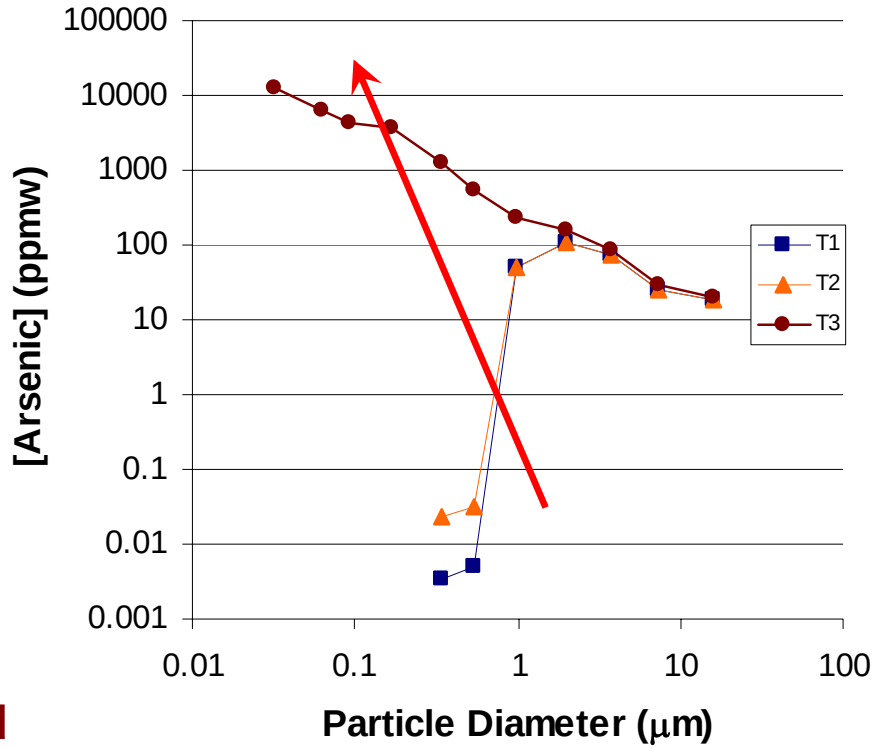
# *Varying Quench Rate*

- Kentucky Coal
  Port 4, Run 4
  - Vaporized metal fraction = 50%
  - Surface area factor = 1



# Concentrations down the Reactor




**T3 = extrapolated to 300K**

**Arsenic remaining in the vapor phase (% of total As)**

| T1 | T2 | T3 |
|---|---|---|
| 70% | 70% | 8.7% |

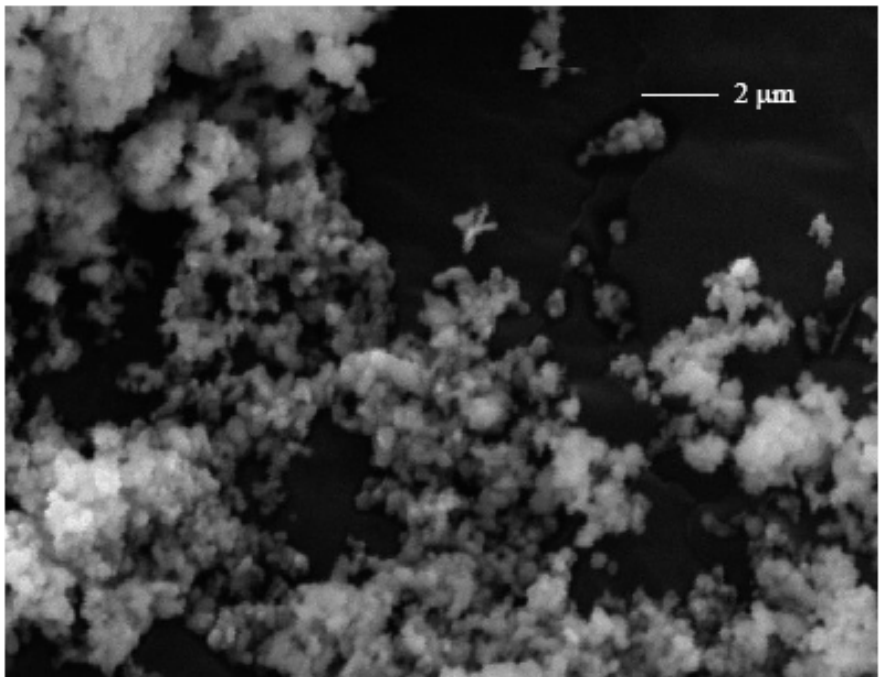
# *Approach: Laboratory*

- Determining Surface Reaction Rates
  - Synthetic fly ash materials
  - Trace metals

- Suspected reaction participant
  - $\alpha$-$Fe_2O_3$
  - $\gamma$-$Fe_2O_3$
  - CaO

- Negative controls
  - Kaolinite
  - Montmorillonite

# *Characterizing Synthetic Fly Ash*




$\alpha$-$Fe_2O_3$ after particle size sorting

- X-ray diffraction
- Size distribution
  - Optical microscopy
  - SEM microscopy
  - Cascade impaction
- BET $N_2$ Analysis

# *Particle Size Distribution*

- Cascade Impaction

| Sample | Stages with Visible Particles | Sample Weight in Visible Stages (%) | Particle Diameter Range (μm) |
|---|---|---|---|
| CaO | 6-9 | 77.6 | 0.2-2.1 |
| $\alpha$-$Fe_2O_3$ | 5-9 | 60.7 | 0.06-1.6 |
| $\gamma$-$Fe_2O_3$ | 2-9 | 75.5 | 0.04-2.3 |
| Kaolinite | 5-9 | 67.0 | 0.1-2.4 |
| Montmorillonite | 7-9 | 60.5 | 0.6-2.7 |

- BET $N_2$ Analysis

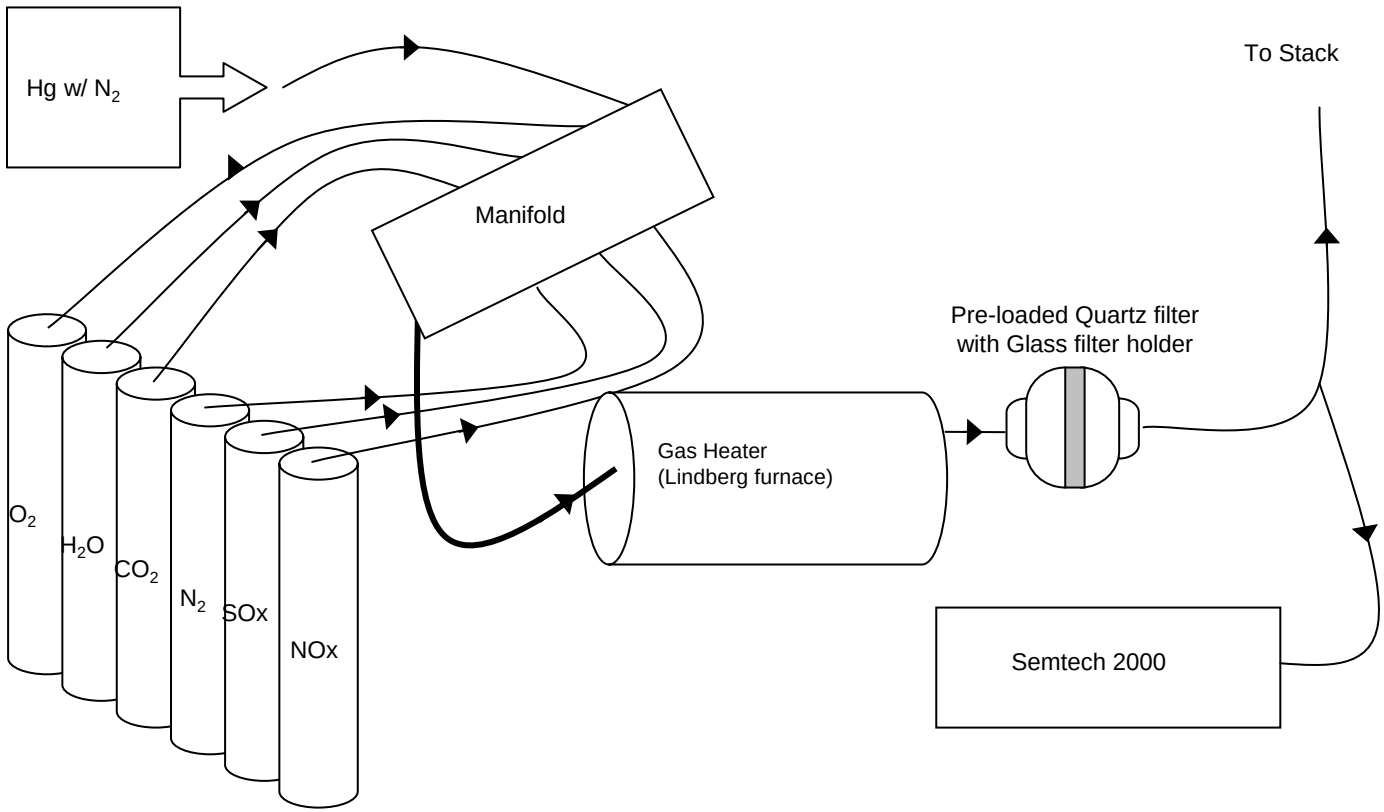
| Sample | Surface area ($m^2/g$) |
|---|---|
| CaO | 11.9 |
| $\alpha$-$Fe_2O_3$ | 5.1 |
| $\gamma$-$Fe_2O_3$ | 7.9 |
| Kaolinite | 26.3 |
| Montmorillonite | 28.9 |

# *Status*

- Dynamic model structured and running
- Ability to predict:
  - *concentration distributions*
  - *remaining vapor fraction*
  - *effect of T gradients*
- Examine importance of surface reaction
- Account for non-vaporized fraction
- Questions regarding vaporization, surface reaction rates remain

# *Future Work*

- Surface Reaction Rates for suspected dominant reactions
  - Arsenic with Iron Oxides
  - Are Ca – As values reported in literature accurate?
  - If so, is surface reaction feasible?

- Expand model
  - Cover additional coal types
  - Examine additional metals volatile at Tc, lower $P^{sat}$
  - Hg

# Bottled Gas Fixed Bed System